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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

Effective Dates: June 1, 1991 to May 31, 1992

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

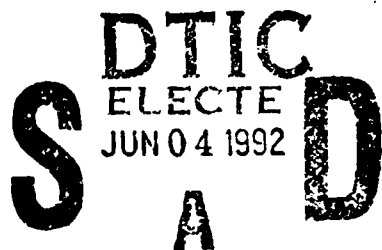
Contract N00014-88-K-0451

R&T Code 4135017

**Macrocyclic Polycation Complexes for Secondary Anion Binding, Molecular Recognition,
and Catalysis**

Arthur E. Martell, Principal Investigator

Texas A&M Research Foundation



**Box 3578
College Station, Texas 77843**

Date submitted: May 31, 1992

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PART I

R&T Number : 4135017
 Contract Number : N00014-88-K-0451
 Contract Title : *Macrocyclic Polycation Complexes for Secondary Anion Binding, Molecular Recognition, and Catalysis*
 Principal Investigator: Arthur E. Martell
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- a. Number of papers submitted to refereed journals, but not published: 3
- b. Number of papers published in refereed journals (list attached): 2
- c. Number of books or chapters submitted but not yet published:
- d. Number of books or chapters published (list attached): 2
- e. Number of printed technical reports & non-refereed papers (list attached):
- f. Number of patents filed:
- g. Number of patents granted (list attached):
- h. Number of invited presentations at workshops or professional society meetings: 1
- i. Number of contributed presentations at workshops or professional meetings: 1
- j. Honors/Awards/Prizes for contract employee (list attached):
- k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number:
 Graduate Students:
 Postdoctoral associates: 3
 including the number of,
 Female Graduate Students:
 Female Postdoctoral Associates:
 the number of
 Minority Graduate Students:
 Minority Postdoctoral Associates:
 and, the number of
 Asian Graduate Students:
 Asian Postdoctoral Associates:
- l. Other funding (list attached): 4

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a. Papers submitted to Refereed Journals (and not yet published)

1. Ramunas J. Motekaitis and Arthur E. Martell
"Molecular Recognition by Protonated O-BISDIEN and Its Metal Complexes", *Inorg. Chem.*, submitted (Technical Report No. 13).
2. S. Cezar, Bruno Szpoganicz and Arthur E. Martell
"Molecular Recognition in the Oxidation of Catechols by Dicobalt-BISDIEN Dioxygen Complexes", *J. Coord. Chem.*, submitted (Technical Report No.14).
3. David A. Rockcliffe and Arthur E. Martell
"Oxidation Reactions of a Binculear Copper(I) Dioxygen Complex, *Inorg. Chim. Acta*, submitted (Technical Report No.).

b. Papers Published in Refereed Journals

1. Rached Menif, Joseph Reibenspies and Arthur E. Martell
"Synthesis, Protonation Constants, and Copper(II) and Cobalt(II) Binding Constants of a New Octaaza Macrobicyclic Cryptand: MX₃TREN₂. Hydroxide and Carbonate Binding of the Dicopper(II) Cryptate and Crystal Structures of the Cryptand and of the Carbonato-Bridged Dinuclear Copper(II) Cryptate", *Inorg. Chem.*, 30, 3446-3454 (1991) (Technical Report No. 5).
2. M. Patrick Ngwenya, Dian Chen, Arthur E. Martell and Joseph Reibenspies
"Oxygenation of a Copper(I) Complex of a Binucleating Macrocyclic Schiff Base Ligand Derived from 1,4,7-Triazaheptane and Furan-2,5-Dialdehyde", *Inorg. Chem.* 30, 2732-2736 (1992) (Technical Report No. 11).
3. Rached Menif, Arthur E. Martell, Philip J. Squattrito and Abraham Clearfield
"New Hexaaza Macrocyclic Binucleating Ligands. Oxygen Insertion with a Dicopper(I) Schiff Base Macrocyclic Complex", *Inorg. Chem.*, 29, 4723-4729 (1990) (Technical Report No.8).
4. Ramunas J. Motekaitis and Arthur E. Martell
"A New Catalytic System for Activation of Molecular Oxygen within the Cavity of a Dinuclear Macrocyclic Complex; the Redox Reaction of the μ -Mesoxalate- μ -Peroxo Dicobalt BISDIEN Complex", *Inorg. Chem.*, 30, 694-700 (1991) (Technical Report No.10).

d. Book chapter published

1. Arthur E. Martell
"Preorganization and Molecular Recognition in Binuclear Macrocyclic and Macrobicyclic Complexes", in *Crown Compounds, Towards Future Applications*, Ed. S. R. Cooper, VCH Publishers, 1992 (Technical Report No.12).
2. Arthur E. Martell and Ramunas J. Motekaitis

"Binding and Activation of Molecular Oxygen within the Cavity of the Dinuclear Reducing Substrates", in *Dioxygen Activation and Homogeneous Catalytic Oxidation*, Ed. L. I. Simandl, Elsevier 1991 (Technical Report No.9).

h. Invited Presentations

"Dioxygen Activation and Transport by Dinuclear Copper(I) Macrocyclic Complexes", Symposium on Copper Coordination Chemistry: Bioinorganic Perspectives, Baltimore, Maryland, August 4-7, 1992.

i. Contributed Presentations

1. "A New Catalytic System for Activation of Molecular Oxygen within the Cavity of a Dinuclear Macrocyclic Complex; the Redox Reaction of the μ -Mesoxalate- μ -Peroxo Dicobalt BISDIEN Complex", European Research Conferences 1991 Series, Strasbourg, France, July 5-8, 1991.

k. Graduate Students and Postdoctorals Receiving Full or Partial Support on this ONR Contract

Graduate Students: ____

Postdoctoral Associates: 3

Minority Postdoctoral Associates: 1

l. Other Funding (note: funding amounts are for current year only.)

The Robert A. Welch Foundation, "Metal Chelate Compounds in Homogeneous Catalysis", \$36,455, 6.1.89-5.31.92,

National Institute of Standards and Technology, "Critical Stability Constants and Related Thermodynamic Constants of Metal Complexes", \$35,000, 4.1.91-3.31.92.

National Institutes of Health, "Development and Testing of New Chelators", \$73,206, 5.1.90-4.30.94.

ARI Technologies, "Research in Iron Complexes of Interest as Catalysts for the Oxidation of H₂S by O₂", \$44,899, 10.14.91-10.13.92.

National Institutes of Health, "Targeted Metal Chelators for Diagnostic Imaging", \$74,068, 4.1.92-3.31.97

PART II

a. Principal Investigator

Arthur E. Martell, Distinguished Professor of Chemistry

b. Current Telephone Number: (409) 845-5055

c. Cognizant ONR Scientific Officer

Dr. Ronald A. De Marco
Director, Chemistry Division

d. Brief Description of the Project

The objective of this research project is to synthesize binuclear cobalt(II) and copper(I) complexes of macrocyclic and macrobicyclic ligands, in which the metal ions are coordinated and held apart at distances such as to recognize and coordinate secondary bridging groups and by so doing activate the bridging groups for redox reactions or increasing the nucleophilic character of the groups to catalyze the rates of substitution reactions. The strengths of binding of the secondary bridging anions or molecules will depend on their ability to coordinate to the two metal centers simultaneously. In other words, the bridging groups should be the correct size and shape to coordinate the metal ions readily. The strength of binding of the secondary bridging groups will be determined from the equilibrium constants involving the combination of these groups with the metal ions, determined potentiometrically and spectrophotometrically.

A specific purpose of this research project is to activate dioxygen by forming a binuclear (peroxo) complex in which the dioxygen is partially reduced and the metal ions are partly oxidized to the next higher valence state. The dioxygen is thus activated for reaction with a second reducing bridging group or an outside reductant which may be added to the system. In cases where the metal ion is incompletely coordinated by the dioxygen bridge and the macrocycle another secondary bridging group may combine with the metal. If this secondary group is also a reductant then it is possible to determine whether or not a redox reaction occurs between the bridging dioxygen and the bridging reductant within the macrocyclic complex. This type of reaction has already been achieved with oxalate and mesoxalate as secondary bridging groups and their reactions to produce carbon dioxide in water have been described. Further reactions of this type will be investigated. Also the ability of Cu(I) to activate dioxygen so that it will react with various reducing agents will be investigated.

e. Significant results during last year

During the past year a full year of work was not possible because of the time required for the conversion of the previous contract to the current research grant. During this period Dr. David Rockcliffe continued his investigation of the Cu(I) macrocyclic complexes for the activation of dioxygen. The work of Dr. R. J. Motekaitis on the redox reactions occurring in binuclear cobalt BISDIEN complexes between coordinated dioxygen and a coordinating bridging reductant was interrupted for several months. However, that work will now be resumed under the new research grant.

Dr. David Rockcliffe has found that the Schiff base formed from the condensation of two moles of furan-2,5-dialdehyde and two moles of diethylenetriamine forms a Cu(I) dioxygen complex with a measurable lifetime at room temperature. The reactivity of the dioxygen complex thus formed with various reducing substrates was measured both in the presence of excess dioxygen, which was found to produce a catalytic cycle, and stoichiometrically in the presence of equal amounts of dioxygen complex and reducing substrate. Thus the rates of reactions and degree of oxygen activation for the Cu(I) complex were determined from the stoichiometric reactions. The Cu(II)

complexes were also investigated and the rates at which they oxidize the same substrates were determined. When these two oxidation reactions are combined a catalytic cycle was formed in which the Cu(I) dioxygen complex oxidized the substrate. In the presence of additional substrate the Cu(II) complex thus formed was reduced to the Cu(I) complex which in turn combined again with dioxygen to form the Cu(I) dioxygen complex in which the oxygen was activated for further reaction, thus both catalytic and stoichiometric oxidation reactions were investigated and a reasonable mechanism for the reactions has been suggested. This work is being written up and should be submitted for journal publication in June 1992.

The work of R.J. Motekaitis on the combination of binuclear Co(II) complex of BISDIEN with a number of bridging molecules or anions was recently submitted to *Inorganic Chemistry*. The affinities of the bridging substrates for the cobalt BISDIEN complexes were determined potentiometrically. The bridging groups investigated are hydrogen phosphate, malonate, glycine, phosphonoformic acid, glycolic acid and acethydroxamic acid. The complexes formed with some of these bridging groups were also found to form dioxygen adducts so that tribridged binuclear cobalt BISDIEN complexes were reported. The bridging groups are the reducing substrate, the dioxygen (as peroxy) and a hydroxo bridge.

f. Brief summary of plans for the coming year

Dr. David Rockcliffe will follow up his initial work on the activation of dioxygen by the Cu(I) complex of the furan containing macrocycle by the use of addition substrates. Some of the substrates selected for this proposed investigation are not readily oxidized by Cu(II) thus leaving only the Cu(I) dioxygen complex as a probable oxidant. The results of the proposed investigation should be very interesting and would provide additional information on the mechanism of the reaction and on the activation of dioxygen by Cu(I). Other reactions to be investigated by Dr. Rockcliffe subsequently will involve the activation of dioxygen adducts of Cu(I) complexes in which the ligand has been varied considerably from the furan derivative to Schiff bases containing pyridine and pyrrole bridges. Also to be investigated is a Cu(I) dioxygen complex reported some time ago by Kida for which the activation of dioxygen toward reaction with reducing substrates has not yet been determined.

Dr. R. J. Motekaitis will be investigating the tribridged complexes of bicobalt(II)-BISDIEN, in which one of the bridging groups is a coordinated dioxygen (written as peroxy group) and one of the others is a reducing substrate. Some of the bridged complexes are recently reported in the paper just submitted to *Inorganic Chemistry* were found to combine with dioxygen. The rates of reaction between the bound dioxygen and the reducing bridging groups will be investigated and the rates of formation of the reaction products will be determined. Also, the binding of additional bridging groups to the cobalt centers will be investigated. Some of these groups are sulfite, phosphite, and α -hydroxy acids. If such groups bind, the possibility of oxidizing them with dioxygen bound within a cobalt macrocyclic complex will be investigated.

It is to be emphasized that the above systems selected for study are unique. This is the only research group that has reported the redox reactions between a bound bridging reducing substrate and a bridging coordinated dioxygen within a macrocyclic complex. Also the oxidation of the various substrates by copper-dioxygen complexes is unique for various reasons: 1, not very many copper-dioxygen complexes have ever been reported and 2, the extent to which copper(I) can activate dioxygen toward reaction with reducing substrates is a subject which has not been thoroughly investigated and further work in this area is needed.

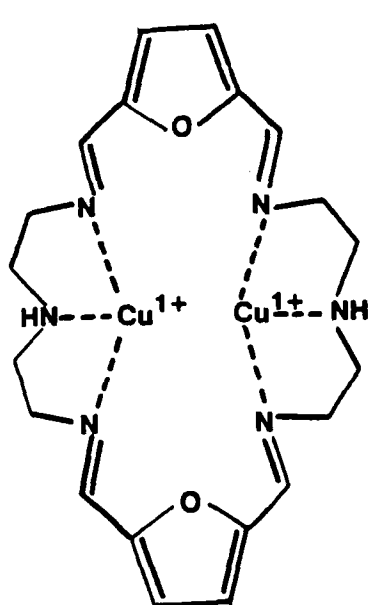
g. List of graduate students and postdoctorals currently working on the project

1. Dr. David A. Rockcliffe, Postdoctoral Research Associate
2. Dr. Ramunas J. Motekaitis, Senior Postdoctoral Research Associate

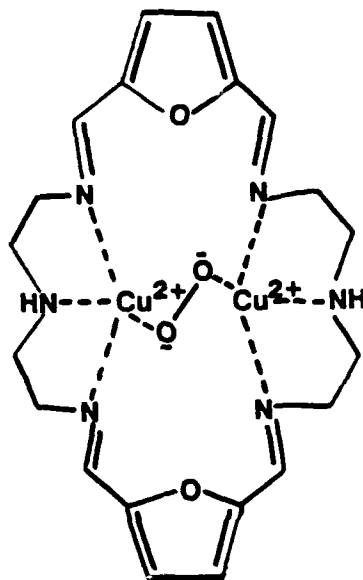
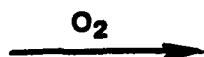
PART III

IIIA Introductory "vu-graph"

Formation and Degradation of a Copper(I) Macrocyclic Complex

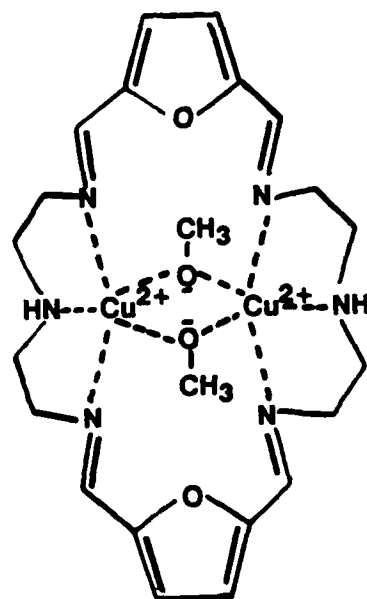


1 Cu(I) Complex



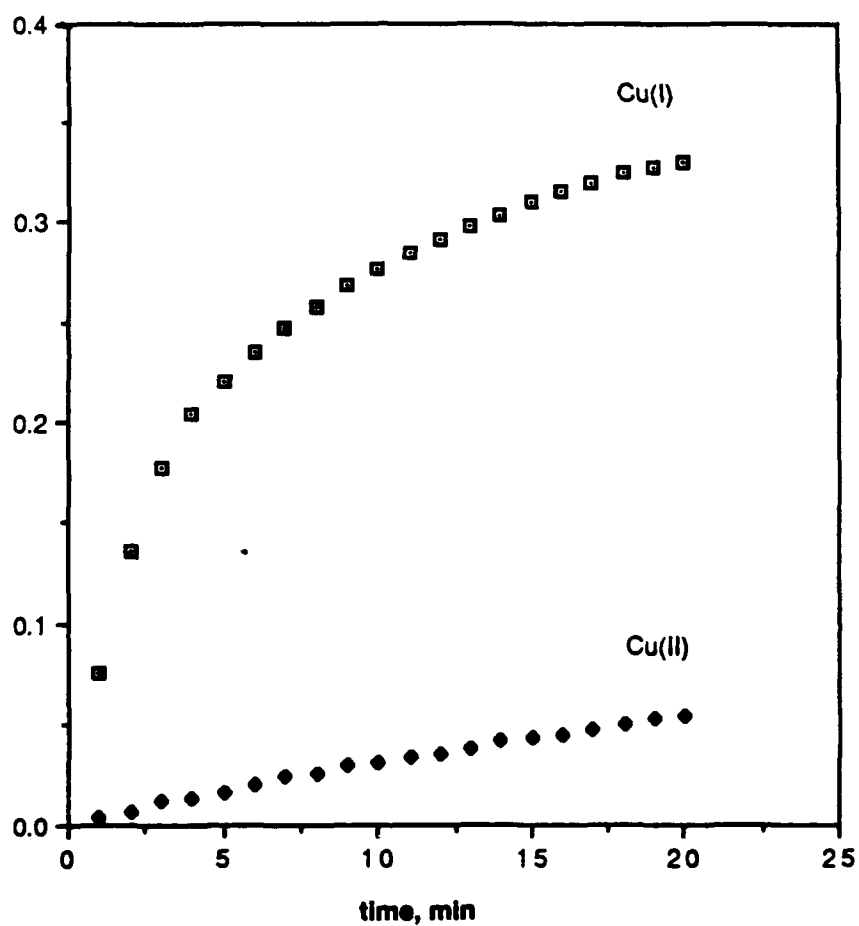
2 Copper Dioxxygen Complex

Degradation



3 Copper(II) Complex

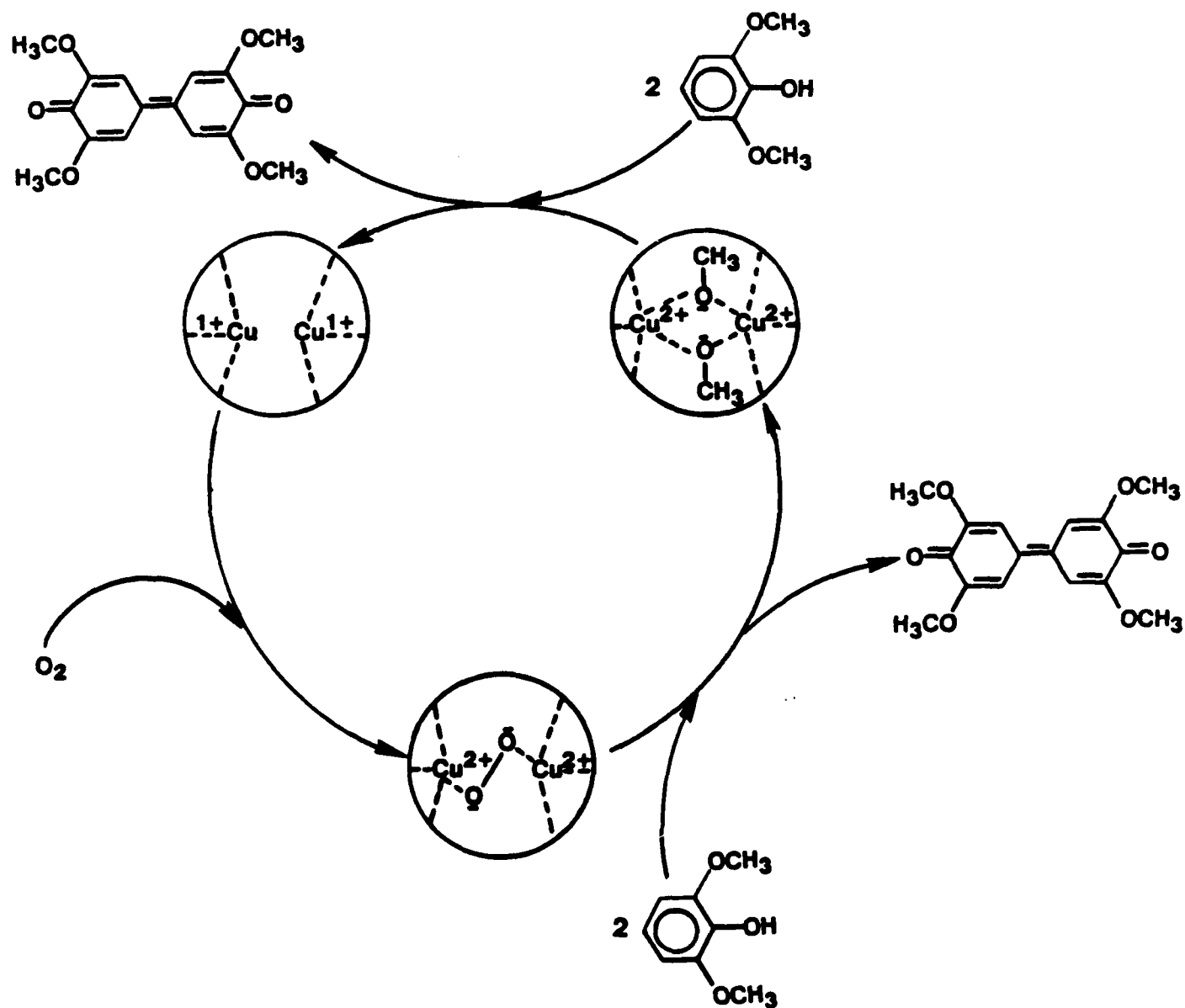
IIIB Figure



Oxidation of 2,6-dimethoxyphenol to 3,3',5,5'-tetramethoxydiphenoquinone by a dinuclear Cu(I) dioxygen complex and by the corresponding dinuclear Cu(II) complex

IIIC Concluding "vu-graph"

Proposed Catalytic Cycle for the Oxidation of 2,6-dimethoxyphenol



IIIId Explanatory Narrative

The catalytic oxidation of various substrates (such as 2,6-dimethoxyphenol) by the dioxygen adduct of the binuclear Cu(I) complex, 2, of the macrocyclic tetra Schiff base ligand containing furan bridges requires that the oxidation reaction occur with both the binuclear Cu(I)-dioxygen complex and with the binuclear Cu(II) complex, 3, as oxidants. The current interpretation is that the Cu(I)-dioxygen complex activates the dioxygen, resulting in a two-electron oxidation of the substrate and the formation of a binuclear Cu(II) complex. The latter may then oxidize a second mole of substrate, to reform the binuclear Cu(I) complex, 1. If additional oxygen is present, the dioxygen complex, 2, may form again and the cycle is then repeated.

To study these reactions in greater detail, the stoichiometric redox reactions of each substrate with both oxidants were carried out. The dioxygen adduct of the binuclear copper(I) complex was formed and all excess dioxygen was removed. The Cu(I) dioxygen complex was then used stoichiometrically to carry out the oxidation of the substrate. In separate experiments the copper(II) complex of the macrocyclic ligand was formed and used as a two-electron oxidant for the same substrate. Comparison of the initial rates of oxidation by the copper(I) dioxygen complex and by the copper(II) complex showed that the oxidation by the dioxygen complex occurs much more rapidly in all cases. Figure 1 illustrates the rates of oxidation of 2,6-dimethoxyphenol to the corresponding diphenoquinone by the Cu(I)-dioxygen complex and by the Cu(II) complex.

The substrates and their corresponding oxidation products studied thus far are:

| | |
|---------------------------|--|
| hydroquinone | quinone |
| tertiarybutylhydroquinone | tertiarybutylquinone |
| 2,6-ditertiarybutylphenol | 3,3',5,5'-tetratertiarybutyldiphenoquinone |
| 2,6-dimethoxyphenol | 3,3',5,5'-tetramethoxydiphenoquinone |
| ascorbic acid | dehydroascorbic acid |